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POLYVINYL ALCOHOL-CLAY COMPLEXES FORMED BY DIRECT SYNTHESIS‡

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Abstract—Synthetic hectorite clay minerals were hydrothermally crystallized with direct incorporation of a series of five water-soluble polyvinyl alcohols (PVA) of molecular weights from 9000–146,000. The molecular weight of PVA had little effect on the success of hydrothermal hectorite synthesis, d-spacing or the amount of polymer incorporated. The basal spacings range from 19.5 Å to 20.8 Å and the amount of polymer incorporated ranges from 20 wt.% to 23 wt.%. Incorporation of PVA within the clay interlayers, along with Li(I) ions to compensate the lattice charge, is indicated. Thermal gravimetric analysis and small angle neutron scattering were used to further examine the polymer-clay systems. Small PVA-clay crystallites that are coated with excess PVA are indicated. Removal of the polymer does not alter the extended synthetic clay network, and the nitrogen BET surface area increases from <5 m^2/g to >200 m^2/g.

Key Words—Clays, Direct Synthesis, Hectorite, Hydrothermal Crystallization, Polymer Clays, Polyvinyl Alcohol, PVA.

INTRODUCTION

Polymer-clay suspensions and composites have considerable commercial and technological importance (Chang et al. 1991). Adsorption on clays of such polymers as polyethylene oxide (Wu et al. 1993; Aranda et al. 1992; Ruiz-Hitzky et al. 1990), polystyrene (Kato et al. 1981), nylon (Kato et al. 1979), polyacrylamide (Schamp et al. 1973) and polyvinyl alcohol (PVA) (Greenland 1963) has been reported. The fundamental chemistry of such interactions has been well documented (Wu et al. 1993; Aranda et al. 1992; Theng 1982; Theng 1979). There are now new reports concerning the nature of polyimide-clay complexes (Lan et al. 1994) and the adsorption of water-soluble cellulosic polymers (Chang et al. 1991) and PVA (Chang et al. 1991; Suzuki et al. 1992) on various clay minerals. As a result of the current climate stressing the development of advanced materials, there are also recent reports of *in situ* intercalative polymerization processes (Messersmith et al. 1993) and some unique structural and electrical properties (Wu et al. 1993; Ogawa et al. 1994; Okada et al. 1990) of polymer-clay composites. Microporous materials based on inorganic matrices and carbonized polymers have been described by Bandosz and co-workers (Bandosz et al. 1992a, 1992b, 1993; Putyera 1994). All of these studies, however, involve modification of an existing clay mineral by such methods as ion-exchange, *in situ* intercalative polymerization or simple adsorption from solution. We have undertaken the exploration of a new avenue of preparation, which is direct hydrothermal crystallization from a polymer-containing silicate gel. The only previously successful report utilizing this method concerns a non-clay layered metal silicate hydrate (Schwieger et al. 1991). This approach may lead to new composite materials with unique properties not possible by natural clay modification.

We have previously reported a method for hydrothermally synthesizing hectorites with direct incorporation of organic or organometallic pillaring agents (Carrado et al. 1994). Hectorites are smectite 2:1 layered Mg silicate clays with cation exchange properties. This general technique of direct synthesis has been used to incorporate water-soluble porphyrins and metalloporphyrins (Carrado et al. 1991), phthalocyanines (Carrado et al. 1993), cationic dye molecules and organometallic complexes (Carrado 1992). Very recently, the effects of neutral and cationic polymers during hectorite synthesis has been reported (Carrado et al. 1995, 1997). This paper will focus on the unique structural properties of PVA-clays made by direct hydrothermal crystallization.

EXPERIMENTAL

Synthetic Hectorites

Synthetic polymer-hectorites are simply referred to as synPVA. The procedure for hydrothermal crystallization of hectorites is explained by Carrado et al. (1991, 1994). Reactants in the molar ratios of LiF: MgO:SiO_2 0.266:1.00:1.52 were refluxed for 2 d as a

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2 wt.% aqueous slurry. This yields the ideal hectorite composition (Grim 1968). $Ex_{0.66}[Li_{0.66}Mg_{5.34}Si_8O_{20}(OH)_4]$, where Ex = exchangeable monocation. The amount of polymer added was chosen such that if all the polymer was incorporated into the clay and assuming complete reaction, 20 wt.% of the clay would be organic. The Li^+ ions occur within the lattice as isomorphous substitutions for Mg^{2+}, leaving a negative charge that is carried by the basal oxygen surface and compensated for by the presence of hydrated exchangeable cations within the interlayer or gallery. In the inorganic synthetic hectorite, Li^+ is also the exchangeable cation. A certain amount of these Li^+ ions can be replaced by organic or organometallic cations directly from a precursor organic-containing gel. The source of MgO was freshly synthesized $Mg(OH)_2$ slurry prepared by precipitation from $MgCl_2 \cdot 6H_2O$ in dilute NH_4OH followed by numerous washings. The source of silica was Ludox HS-30. To isolate the clay, the slurry was centrifuged and washed three times or until the decant was clear, allowed to air-dry, then powdered. Thin films were made by drying some of the washed slurry on a glass slide.

Materials

Ludox HS-30, a Na^+-stabilized 30 wt.% silica sol, was obtained from DuPont. All polyvinyl alcohols (PVA) were purchased from Aldrich. PVA polymers of varying molecular weights and hydrolysis percentage were used: MW = 9000–10,000 (88% hydrolyzed), MW = 13,000–23,000 (88% hydrolyzed), MW = 31,000–50,000 (88% hydrolyzed), MW = 50,000 (99+% hydrolyzed) and MW = 85,000–146,000 (88% hydrolyzed). The water used in all experiments was both distilled and deionized.

Modification of natural clays was carried out for comparison with the synthetic clays. The montmorillonite used was Bentolite L™, a Ca^{2+}-bentonite from Southern Clay Products, Gonzales, TX. SHCa-1 is a California Na^+-hectorite distributed by the Source Clays Repository, Columbia, MO. As supplied, it contains approximately 50% $CaCO_3$ and iron-containing impurities that were removed by sedimentation techniques. A 1 wt.% clay slurry was charged with enough polymer to cause 20 wt.% organic assuming full adsorption. The slurry was stirred overnight at room temperature, then centrifuged, washed and air-dried. The slurry must first be heated to 50 °C for 30 min to insure that the PVA polymer is fully dissolved. Another natural Na^+-hectorite called Hectabrite AW, from American Colloid Co., Arlington Heights, IL, was used for the X-ray powder diffraction (XRD) comparison with synthetic hectorites. Hectabrite AW is an already purified form of a natural hectorite and has less impurities than SHCa purified in the lab. Calcination of polymer-clays was carried out in a tube furnace using quartz boats at 400 °C under air or oxygen flow for at least 4 h.

Characterization

XRD analyses were carried out on a Scintag PAD-V instrument using Cu-Kα radiation and a hyperpure germanium solid-state detector at a scan rate of 0.5 °2θ/min. The instrument was calibrated to the (101) reflection of low-quartz at 3.34 Å. Powders were either loosely packed in horizontally held trays or spread out on glass slides. Thermal gravimetric analysis (TGA) was performed either on a CAHN-121X in an oxygen atmosphere (40 ml/min) with a heating rate of 10 °C/min or on a TA Instruments SDT 2960 simultaneous TGA-DTA (differential thermal analysis) under an oxygen flow of 100 ml/min. N_2 BET surface area measurements were collected on a Quantasorb Jr. sorption analyzer after outgassing at room temperature under N flow overnight. Measurements were also made on an Autosorb-6 to obtain more detailed adsorption/desorption behavior. SANS measurements were made at the Intense Pulsed Neutron Source at Argonne National Laboratory, IL. Experimental conditions are published elsewhere (Carrado et al. 1991). The powders were held in 1 mm quartz cells.

RESULTS

The XRD pattern of synLi, a synthetic hectorite with Li^+ exchangeable cations (no polymer), in the powder form is shown in Figure 1b. This typical pattern of all the synthetic hectorites shows a basal or (001) spacing of 14.3 Å (6.18 °2θ). This value includes the thickness of the clay layer, which is 9.6 Å for a typical smectite (Grim 1968). The peak at 4.30 Å (20.5 °2θ) represents the (110) and (020) reflections of clay and the 2.56 Å peak (35.6 °2θ) represents the (130) reflection of clay. Note that there is no sign of unreacted $Mg(OH)_2$, which would display peaks at 4.77 Å (18.6 °2θ) and 2.37 Å (38.0 °2θ) for the (001) and (101) reflections of the magnesium hydroxide mineral brucite. For comparison, the XRD pattern for a natural hectorite is shown in Figure 1a. This demonstrates the similarity of peak widths and intensities of hk reflections for both natural and synthetic minerals. This natural hectorite, even though extensively purified, still contains some $(Mg,Fe)SiO_3$ as indicated by the asterisks. Figure 1c shows the XRD pattern synPVA. Note the typical hk clay reflections and the increase in basal spacing with PVA uptake.

The (001) spacings, the amount of intercalant incorporated and surface areas before and after calcination are listed in Table 1. The polymer loadings were calculated from the wt.%C and the known molecular formula (PVAOH is 54.5 wt.%C). The loadings were also verified by TGA results. The molecular weight of polyvinyl alcohols had little effect upon the d-spacing or amount of polymer incorporated. Therefore, only

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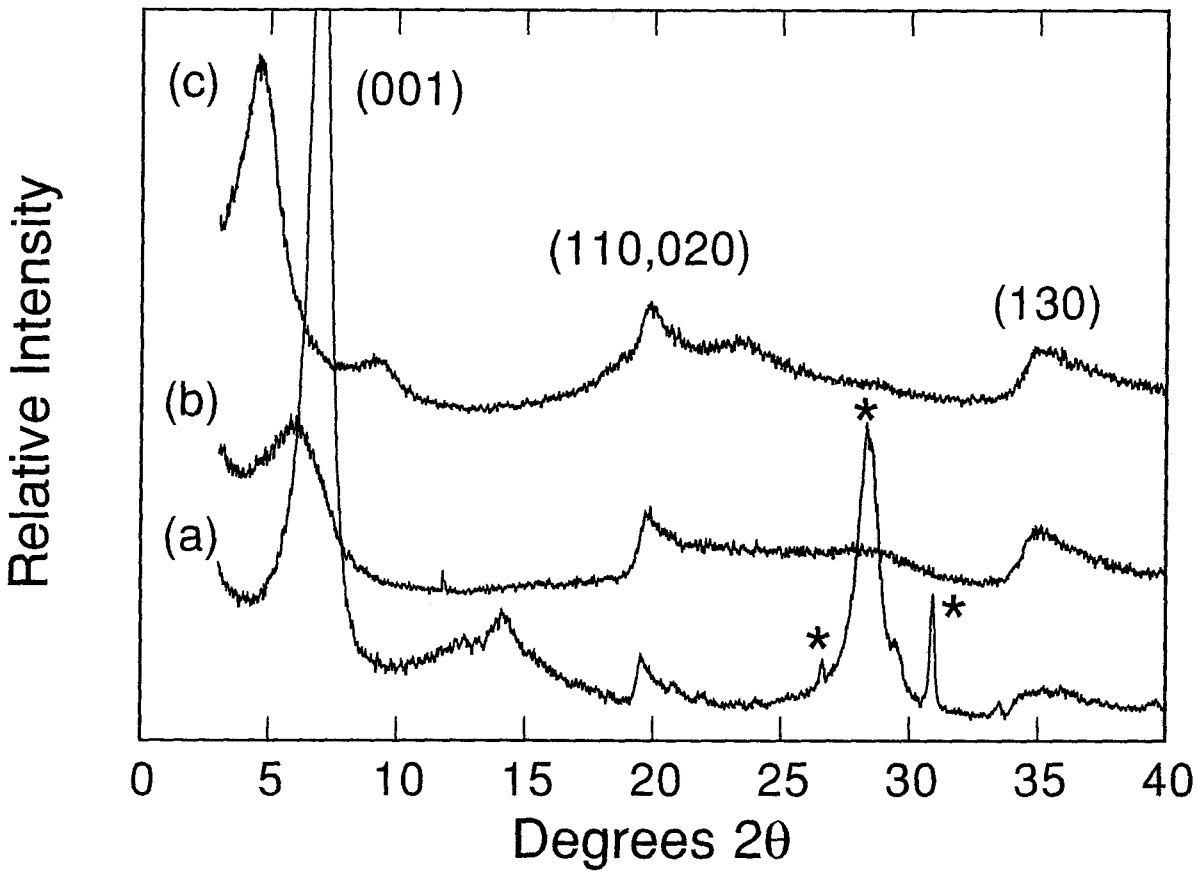


Figure 1. XRD patterns of: (a) natural Na-hectorite; the peaks indicated with an asterisk (*) are due to $(Mg,Fe)SiO_3$ (JCPDS file #19-605); (b) synthetic Li-hectorite; and (c) synthetic PVA-hectorite (PVA MW = 50,000).

one representative PVA sample of MW 50,000 is presented.

A comparison of the synthetic polymer-containing hectorites versus modified natural hectorites was also carried out. The natural hectorites were modified by simple adsorption. Table 1 contains pertinent information for PVA of MW 50,000. The basal spacings and polymer loadings are nearly identical for the natural and synthetic clays. PVA was also adsorbed onto a sample of a natural Ca^{2+}-montmorillonite. This was done to examine the effect of a natural clay's exchangeable cation on polymer uptake. Both montmorillonite and hectorite are examples of clay minerals called smectites, and have virtually identical structures and cation exchange properties. The examples only differ slightly in elemental composition of the framework. The primary difference between these clays lies within their native exchangeable cation, Na^+-hectorite versus Ca^{2+}-montmorillonite. The PVA-hectorites always showed a large degree of both swelling and polymer uptake. This did not occur extensively for the montmorillonites, although heating the suspensions did increase the basal spacing and polymer uptake. This heating effect was not observed for the hectorites (Table 1).

Table 1. Physical properties of PVA-containing clays.[1]

Clay	XRD (001) Å	wt% organic	N_2 BET surface area (m^2/g)	S.A. (m^2/g) after calcination[2]
synthetic Li-hectorite (no polymer)	16.5	—	200	196
synthetic PVA-hectorite	20.4	22.2	<5	283
natural PVA-Na^+-hectorite	19.8	24.2	<5	108
natural PVA-Ca^{2+}-montmorillonite	15.5	8.0	56	96
natural PA-Ca^{2+}-mont., heated[3]	17.0	10.3	n.d.	n.d.

[1] PVA MW = 50,000. The results from all other PVA molecular weights were nearly identical.

[2] Nitrogen BET surface areas measured after heating the complexes at 400 °C for 4 h in O.

[3] This complex was refluxed for 16 h rather than stirred at room temperature, as the others were. n.d. = not determined.

The surface area of synthetic Li-hectorite clay (no polymer) is quite high at 200 m^2/g, indicating that the particle size is small (Carrado 1992). It is well-known

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Table 2. Thermal gravimetric analysis (TGA) data.[1]

Sample[2]	Weight loss region I		Weight loss region II		Ratio of wt% I/II
	Temp °C	wt%	Temp °C	wt%	
pure PVAOH	270, 350	54.4	440	42.0	1.3
synthetic PVA-hectorite	302	12.3	470	13.2	0.9
natural PVA-Na^+-hectorite	280	7.7	460	12.8	0.6
natural PVA-Ca^{2+}-montmorillonite	276	6.6	380	3.3	2.0

[1] Data is for the regions due to decomposition of organic only.
[2] Molecular weight of PVA in all cases is 50,000.

that the smaller sheets present within fine-grained clays pack into smaller stacks, less regularly, so the ratio of external to internal surface area increases (Newman 1987). The surface area of a typical natural smectite clay like hectorite or montmorillonite is about 80 m^2/g. Because the surface areas of the synPVA samples are so low (<5 m^2/g), the possibility of PVA coating the particles was investigated. Removal of the polymer by calcination restores all of the original surface area (Table 1). The percentage of carbon remaining after calcination of synPVA (PVA MW 9000–10,000) is only 0.15%, and the d-spacing (a peak of low intensity) decreases to 10.8 Å. A natural PVA-hectorite behaves similarly to synPVA such that the surface area is low (<5 m^2/g), but is fully restored upon calcination (Table 1). The surface area is enhanced slightly, to 100 m^2/g. This may result from the residual carbon present on the surface (Bandosz et al. 1992b; Putyera et al. 1994). Calcined clays derived from PVA molecular weights 85,000–146,000 display a surface area of 233 m^2/g and a total pore volume of 0.35 cm^3/g.

The thermal decomposition of PVA within its pure form and clay composites is similar, as can be seen from the TGA data in Table 2. Only the weight loss regions due to organic are tabulated for the polymer-clays. Figure 2 compares the weight loss of a typical synPVA to pure PVAOH of molecular weight 50,000. The initial weight loss from 25 to 150 °C for clays is due to surface and interlayer water, and that at 700 to 800 °C is due to dehydroxylation of the clay lattice.

Small angle neutron scattering (SANS) can provide information on the size, shape and interaction of particles in a size range of 10–1000 Å. It also provides information about such properties as the thickness of the clay layers, the relative size of the platelets, correlations between the platelets in terms of their packing, etc. This technique can probe the interaction of polymers with other reactants such as silica, as well as within the final product. SANS data for synthetic hectorites with and without PVA are shown in Figure 3. The curves merge together in the high q region for the prepared, uncalcined samples, thus implying similar structures at smaller length scales. However, data within the low q region exhibit significant differences. The power law slope for synLi is -1.67 ± 0.027 and for synPVA it is -1.37 ± 0.075. The mid-q region "hump" at approximately $q = 0.032$ $Å^{-1}$ is due to aggregated unreacted silica particles with a size of 196 Å. Figure 3 also shows the calcined version of synPVA after burning out of the polymer. Since all of the PVA samples showed similar scattering behavior, only the data for MW = 50,000 is shown. Notice the overall straightening of the curve, especially at high q values, showing the polymers effect on the scattering. Figure 4 displays SANS of a natural hectorite clay both with and without PVA. Error bars are not drawn on any of these plots because, except at very high q-values, they were of smaller or comparable size to that of the data points.

DISCUSSION

Proposed Structures

In order to best understand synPVA, it is beneficial to first summarize the information available on natural PVA-clays. The adsorption of PVA by natural montmorillonite is influenced by the exchangeable cations' nature and by ionic strength (Theng 1982). Exchangeable cations affect the degree to which a clay will swell in aqueous solution (Barrer 1978), which is an obvious factor regarding polymer adsorption. The reported complex with Na-montmorillonite at maximum adsorption (Greenland 1963) (ca. 80 wt.%) has a basal spacing of 30 Å (gallery height 20 Å). This has been attributed to two flat, extended monolayers of PVA within the gallery (Theng 1982) of an average loop length of 10 Å for each chain. Another case of bimolecular coverage of a polymer within clay galleries has been shown for poly(vinylpyrrolidone) within Na-tetrasilicic mica (Ogawa et al. 1993). However, Ca^{2+}-smectites do not swell to as large a degree as the Na^+-analogs (Barrer 1978). This phenomenon is borne out by the results of PVA-montmorillonite (Table 1). The d-spacing is considerably less for the Ca^{2+}-montmorillonite, although it increases upon heating the polymer-clay slurry. This heating effect upon d-spacing is not observed for the Na^+-smectites loaded with PVA because the clay layers are already swollen macroscopically.

The coverages observed for the synPVA samples are at approximately ¼ of the full-loading reported

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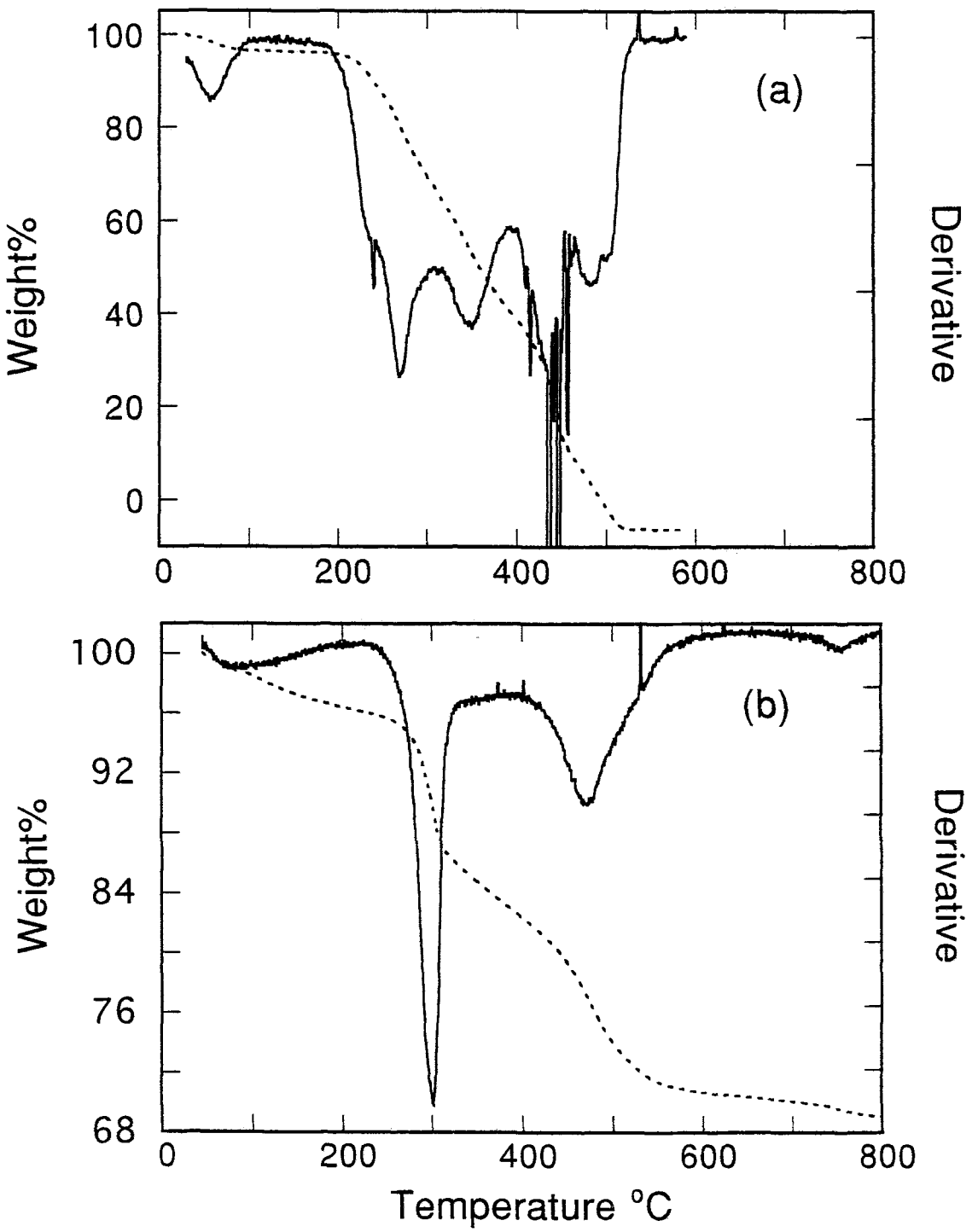


Figure 2. Thermal gravimetric analysis curves for (a) PVAOH (MW 50,000) and (b) synthetic PVA-hectorite (MW 50,000): (– – –) weight% (——) derivative.

above. The gallery heights of approximately 10 Å correspond to a single flat extended monolayer of PVA according to the argument of Theng (1982). The most important variable appears to be the degree to which the clay layers swell within solution, which is a factor ultimately controlled by the cation exchange of natural clays. The results reported here indicate that the synthetic clay layers are far apart as they crystallize from

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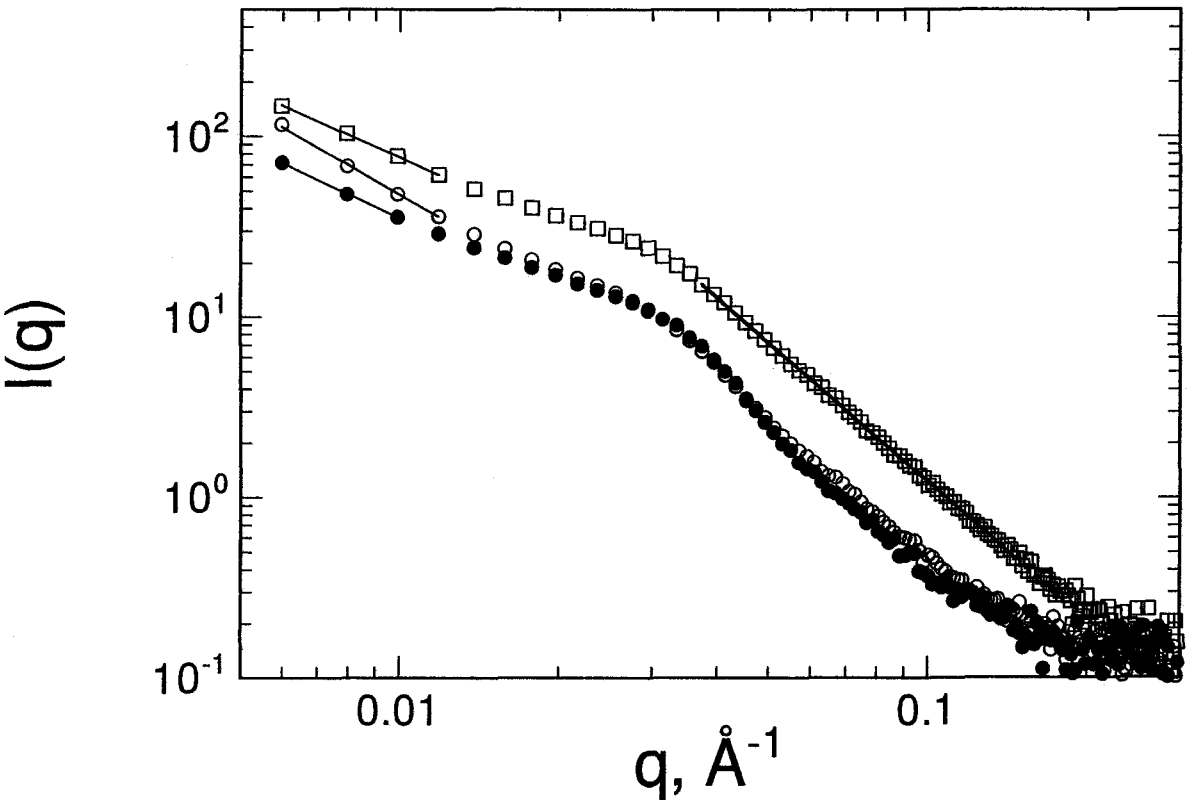


Figure 3. Log I vs. log q plots of the small angle neutron scattering for synthetic hectorite powders containing: Li(I) (ooo) = slope of linear region −1.67 ± 0.027; PVA (·····) = slope −1.37 ± 0.008; PVA (□□□) = after calcination, low-q slope −1.4, high-q slope −2.56 ± 0.005. Error bars are not shown because up to q = 0.1 Å^{-1} they are smaller or of comparable size to the data points. Molecular weight of PVA was 50,000.

a gel, thus providing the polymer ample surface with which to interact. When in the clay interlayer, Li^+ ions, like Na^+ ions, cause macroscopic swelling within water (Newman 1987).

There is some question regarding the exact physical structure of PVA-clay complexes. In contrast to Greenland's (1963) result of 30 Å, Lagaly (1986) reports that a PVA-Na^+-montmorillonite yields a very broad basal reflection. Lagaly postulates that the silicate layers are no longer parallel and are embedded in a gel of PVA and water. Ege et al. (1985) support this scenario by electron spin resonance methods. The high degree of disorder observed by Lagaly (1986) is in fact for samples that are slightly wet and in contact with excess PVA solution. However, after extensive drying in vacuo at 65 °C, a d-spacing of 13.6 Å results. In this PVA-clay complex, with the gallery height of only 4 Å, a single PVA monolayer is less than half of that proposed by Theng at 10 Å. When the interlayer cations are sodium ions, it is apparent that the ordering of the layers and the resultant basal spacing depend strongly upon the degree and method of drying.

The basal spacing of 20 Å that occurs for synPVA is an intense peak that (Figure 1c) shows a higher order (002) reflection, indicating a fairly high degree of ordering. According to the argument of Theng (1982), this value corresponds to a single extended monolayer of PVA within the layers. This is a reasonable assumption for synPVA considering that the samples were simply air-dried at room temperature, not rigorously dried in vacuum or at elevated temperatures.

Other workers support the PVA-clay structure of Greenland (1963). Specifically, Suzuki et al. (1992) studied the adsorption of PVA on Na- and Al-montmorillonites, a synthetic mica and saponite. The reported relationships between d-spacings and % organic uptake suggest an interlayer adsorption. However, the greatest degree of PVA adsorption occurs on saponite at 77% organic, and a "house-of-cards" structure is proposed for this material.

The structures of Greenland and Lagaly are shown schematically in Figures 5a and b, respectively. We propose that aspects of both structures are present in the synthetic PVA-hectorites reported. A simplistic representation is given in Figure 5c. For such a model, PVA exists between the clay layers in a regular fashion without delamination giving rise to the observed basal spacing, but an outside coating of excess PVA

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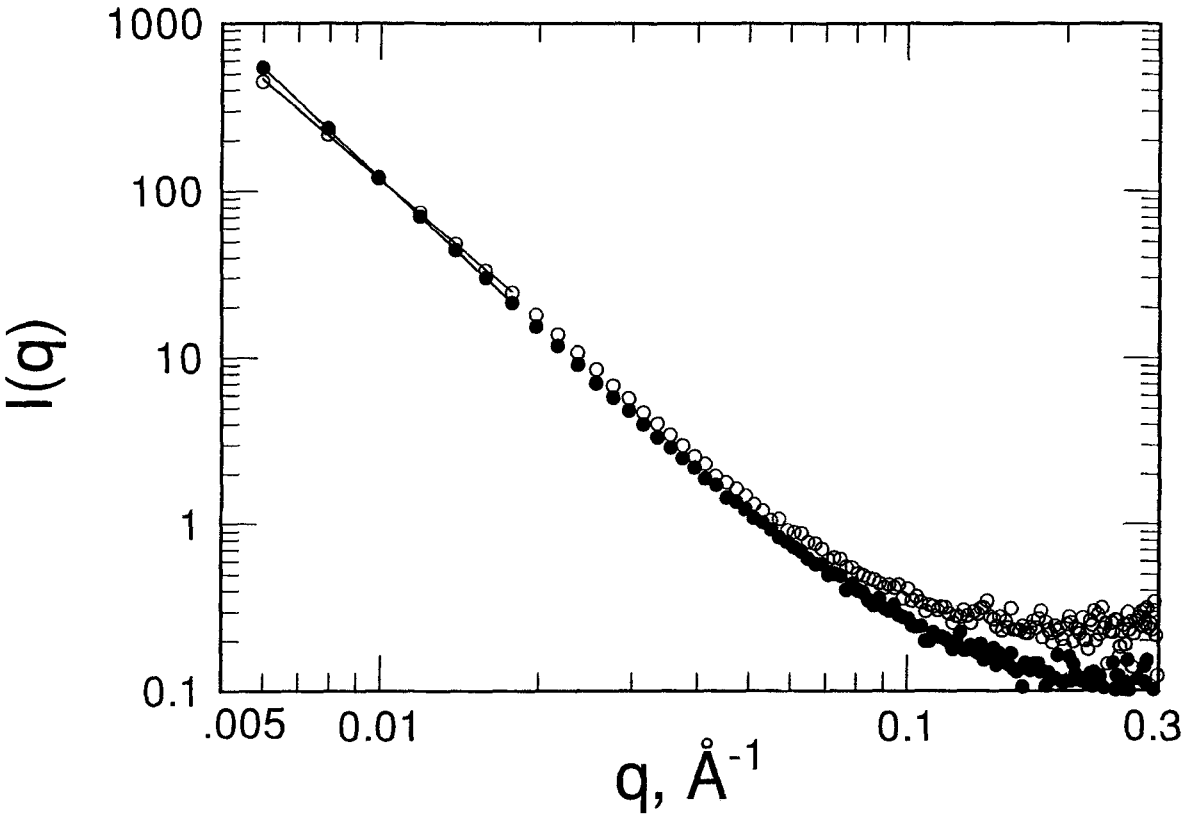


Figure 4. Log I vs. log q plots of the small angle neutron scattering for a natural hectorite clay mineral (●●●) = slope −2.96 ± 0.003, and one treated with PVAOH (MW 50,000) (○○○) = slope −2.76 ± 0.006. Error bars are not shown because up to q = 0.1 $Å^{-1}$ they are smaller or of comparable size to the data points.

hardens on the crystallites. It could be argued that hydrothermal crystallization using lower polymer levels might decrease the amount of "gel" PVA. However, at an anticipated 10 wt.% PVA loading the syntheses actually yielded products similar to those prepared with 20 wt.% polymer. The overall product yields were quite low (20 to 50%), which allowed the non-stoichiometric polymer loading to occur.

For a structure consisting of disordered clay layers embedded in a gel of PVA and H_2O, one would assume that a substantial amount of H_2O would be present. But, the TGA results (Figure 2) did not bear this out for our samples. A pure synthetic hectorite without polymer displays 9.5 wt.% loss up to 200 °C, which is due to surface and interlayer water. The synthetic PVA-hectorites display very similar values within the same temperature region, such as the 9.7 wt.% H_2O for the sample derived from PVA MW 50K. Pure polyvinyl alcohol itself shows about 4 wt.% water for this region. Therefore, the PVA coating is quite dense and probably not really "gel-like" as reported for other PVA-clay models (Lagaly 1986).

Crystal Growth by SANS

In order to see any modification of the extended inorganic network by polymers within the natural hectorites, Figure 4 exhibits SANS of clays with and without PVA. The excess signal in the high q region for the sample treated with PVA is due to the polymer. The power law slopes for natural hectorite with PVA is −2.76 and without PVA is −2.96. The significant decrease of the power law slope for the polymer-clay is due to some intercalation of PVA, decreasing the packing density of clay layers and gelation around the clay particles. For synPVA (Figure 3) this same effect occurs. Specifically, a smaller power-law exponent of −1.37 vs. −1.67 for synLi indicates that PVA may act to coat the clay particle just as it has begun to form, restricting it from further growth. While the clay particles from synLi are also very small, addition of other cationic species to the gel often enhances the growth of the clay crystallites (Carrado et al. 1995, 1997).

To gain information concerning the interaction of the polymers and their disposition within the synthetic clays, SANS studies were also carried out for the calcined powder samples (Figure 3). The size, aspect ratio and packing density of calcined synthetic PVA-clays prepared from PVA with different molecular weights are nearly identical. This means that within the range of PVA molecular weight from 9000 to 146,000 there is no difference in the resulting material.

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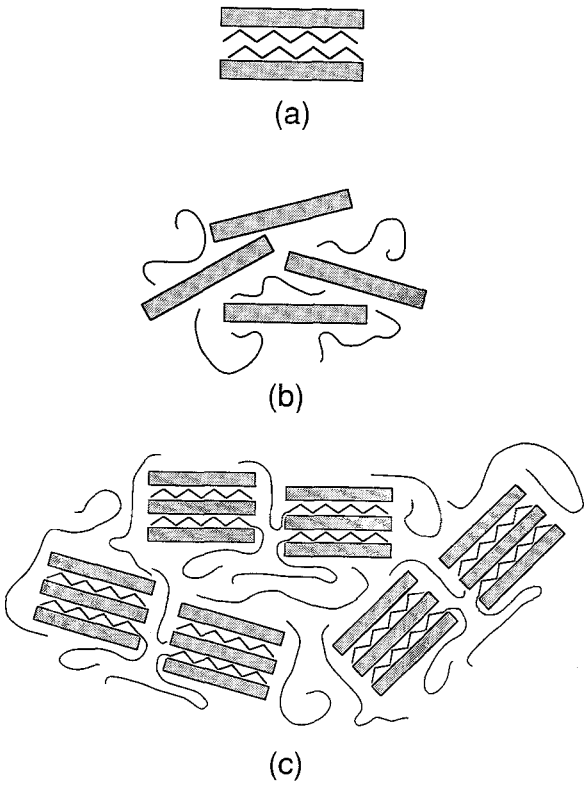


Figure 5. Schematic representations of the proposed PVA-clay complexes of (a) Greenland (1963), with two flat extended monolayers within a Na-montmorillonite with a d-spacing of 30 Å, (b) Lagaly (1986), with delaminated Na-montmorillonite layers within a PVA-gel matrix, and (c) this work, showing a single PVA monolayer within a Li-smectite with a d-spacing of 20 Å within a PVA-gel matrix; the more disordered arrangement of the smaller clay stacks vs. natural clays is indicated.

The small variations within the power law slopes of synPVA from uncalcined to calcined indicate that the extended clay networks are similar and have not been disrupted upon calcination. Nitrogen BET surface areas for synPVAs are low upon preparation but are fully restored after removal of the polymer. The surface area results upon calcination can now be explained. While a certain amount of these neutral polymers have intercalated within the galleries, as seen by XRD, they are also present to some degree as a coating to block access to the internal surface area. The slope at high-q is -2.56, which is much closer to the slopes observed for the natural clays.

CONCLUSIONS

The synthetic PVA-hectorite preparations cause extremely small crystallites to form. Because of their low aspect ratio, it is no surprise that SANS data show that they are not well stacked, even given that enough order is maintained to give a basal spacing in XRD. PVA appears to coat the small initially formed clay particles, hindering their further growth. There is no change to the extended inorganic network upon removal of the polymer, as indicated by small angle neutron scattering results. In general, the feasibility of direct hydrothermal crystallization for the preparation of polymer-layer silicates is demonstrated. This new technique offers the possibility of making materials not possible by modification of existing clay minerals by such methods as ion-exchange, adsorption or polymerization of intercalated monomers.

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